to appear in JMMM (proceedings of JEMS'04) version of 30 June 2004
www.elsevier.com/locate/jmmm

Exchange constants and spin dynamics in Mn_{12}-acetate

A. Honecker [a], N. Fukushima [a,1], B. Normand [b], G. Chaboussant [c], H.-U. Güdel [d]

[a] *Institut für Theoretische Physik, Technische Universität Braunschweig, Mendelssohnstr. 3, 38106 Braunschweig, Germany*
[b] *Département de Physique, Université de Fribourg, 1700 Fribourg, Switzerland*
[c] *Laboratoire Léon Brillouin, CEA-Saclay, 91191 Gif-sur-Yvette Cedex, France*
[d] *Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, 3000 Bern 9, Switzerland*

Abstract

We have obtained new inelastic neutron scattering (INS) data for the molecular magnet Mn_{12}-acetate which exhibit at least six magnetic peaks in the energy range 5–35 meV. These are compared with a microscopic Heisenberg model for the 12 quantum spins localised on the Mn ions, coupled by four inequivalent magnetic exchange constants. A fit to the magnetic susceptibility under the constraint that the spin of the ground state be $S = 10$ yields two dominant exchange constants of very similar value, $J_1 \approx J_2 \approx 65$ K (≈ 5.5 meV), and two smaller exchange constants J_3 and J_4. We compute the low-lying excitations by exact numerical diagonalisation and demonstrate that the parameters determined from the ground state and susceptibility fit provide qualitative agreement with the excitations observed by INS.

PACS: 75.30.Et; 75.50.Xx; 78.70.Nx

Keywords: Magnetic molecular materials; Heisenberg model; Susceptibility – magnetic; Neutron scattering – inelastic

Magnetic molecules present a fascinating new class of materials with a wide variety of applications (for a recent review see [1]). Coherent quantum phenomena in these mesoscopic systems are one focus of recent research [2]. Despite being among the first generation of molecular magnets to be synthesised, Mn_{12}-acetate [3] remains that with the largest barrier to thermally activated tunnelling. Although much work has been devoted to Mn_{12}-acetate over the past decade, the microscopic mechanisms for the observed low-energy phenomena have remained controversial.

Here we discuss a microscopic exchange model for Mn_{12}-acetate. Twelve quantum spins $\mathbf{S}_i$ are coupled by Heisenberg exchange interactions

$$H = \sum_{i,j} J_{ij}\, \mathbf{S}_i \cdot \mathbf{S}_j \qquad (1)$$

with four different exchange constants J_1, J_2, J_3 and J_4, as represented in Fig. 1.

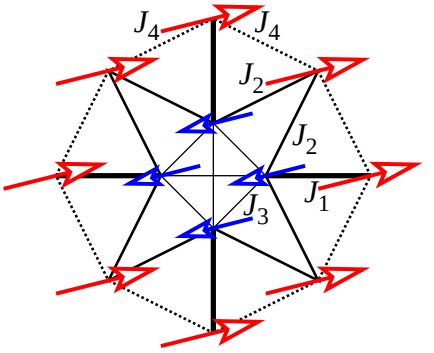

Fig. 1. Magnetic exchange model for Mn_{12}-acetate. Arrows denote the twelve Mn ions: eight Mn^{3+} ions on the crown have local spin $S = 2$ while four Mn^{4+} ions in the core have $S = 3/2$. Lines show exchange paths with interaction parameters J_1, J_2, J_3 and J_4.

Many experimental studies, including inelastic neutron scattering (INS) [4], show that the ground state (GS) of Mn_{12}-acetate has total spin $S = 10$. This may

[1] Present address: University of the Saarland, Theoretische Physik, Geb. 38, 66123 Saarbrücken, Germany

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be rationalised by considering an arrangement of 8 parallel spins $S = 2$ on the crown Mn^{3+} ions oriented antiparallel to 4 aligned $S = 3/2$ spins on the core Mn^{4+} ions (Fig. 1). The $S = 10$ GS imposes a strong constraint on the allowed exchange constants in (1), excluding [5,6] a number of parameter sets proposed in the literature, such as that obtained by the *ab initio* local density approximation [7].

The magnetic susceptibility χ is a valuable quantity in the determination of magnetic exchange constants. Fig. 2 shows two results for χ, measured with an ordinary sample under an applied field of 1 T [8], and with a deuterated sample at 0.1 T [6]. Both data sets agree well for temperatures between 40 and 300 K despite the different conditions, demonstrating the reliability of the susceptibility measurement at high temperatures. Exchange constants can then be determined by comparison with a symbolic high-temperature series expansion. In combination with a numerical test of the $S = 10$ ground-state requirement, this restricts the possible parameters to a narrow region around $J_1 \approx J_2 \approx 60$ K, $J_3 \approx J_4 = 5$–10 K [6].

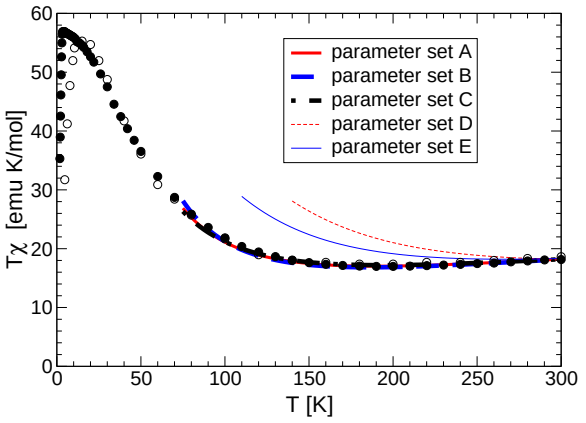

Fig. 2. Static magnetic susceptibility. Filled and open circles are measured respectively on a deutered sample under a field of 0.1 T [6] and on a non-deuterated sample at 1 T [8]. Lines are obtained from an 8th-order high-temperature series for the parameter sets in Table 1.

Columns A, B and C of Table 1 list three choices of parameters in this region (parameter set A was used in [6]). Columns D and E contain the parameter sets proposed in [9] and [10] respectively. The lines in Fig. 2 show the susceptibility χ obtained from an average of four different Padé approximants to the 8th-order high-temperature series [6] evaluated with the corresponding parameters. The last row of Table 1 lists the effective g-factor entering the absolute value of χ (electron paramagnetic resonance [11] yields $g_{\rm eff} = 1.968$). Parameter sets A, B and C yield good agreement with the experimental results, whereas the results for sets D and E are in clear disagreement. We conclude that the exchange constants proposed in Refs. [9,10] are incompatible with χ.

A number of magnetic excitations in the range of 5 to 35 meV has been observed by INS experiments performed on different spectrometers [12,6]. The points in Fig. 3 show the spectrum obtained on the MARI spectrometer at ISIS with an incident energy $E_i = 17$ meV. Five magnetic excitations can be identified unambiguously in this data, and are shown by the lines in Fig. 3, which are fits with Gaussian curves on a linear background. Analysis of their Q- and T-dependence identifies these five excitations as magnetic and at least the lowest two of spin $S = 9$ [6]. A further magnetic excitation at 27 meV is the first candidate for an $S = 11$ excitation [6], in accord with high-field magnetisation measurements; this energy sets a lower bound for the numerical calculations

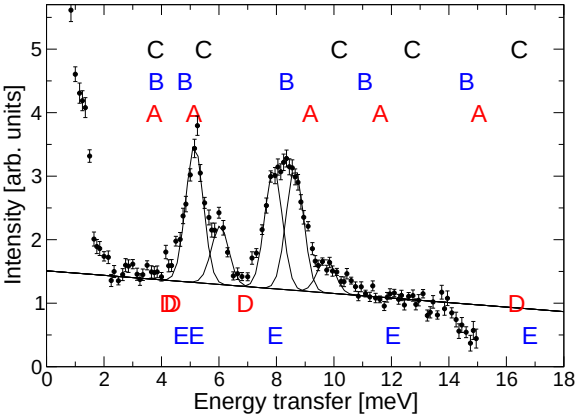

Fig. 3. Magnetic excitations. Points show the INS spectrum obtained on MARI with $T = 8$ K, $E_i = 17$ meV and $1 \le Q \le 2$ Å^{-1}. Lines are Gaussian fits on a linear background. Letters represent numerical results for the $S = 9$ excitations listed in Table 1 for the corresponding parameter choices. A constant energy 1.29 meV has been added to all calculated energies to account for magnetic anisotropy effects [6].

We have performed exact diagonalisation for the model Hamiltonian (1), both to verify the $S = 10$ GS and to determine the low-lying excitations. The lowest excited states in the sectors with spin $8 \le S \le 11$ are listed in Table 1 in ascending order of energy (for sets A, D and E these extend results presented in [6,9,10]). Spatial symmetry is described by a momentum k such that the wavefunction acquires a phase factor e^{ik} under a 90° rotation of the model in Fig. 1. The letters in Fig. 3 show the energies of the lowest $S = 9$ excitations for the corresponding data sets in Table 1. A constant shift of 1.29 meV is added to all computed energies [6] to account for the uniaxial cluster anistropy. Parameter set D [9] provides only 4 instead of the observed 5 levels in the energy range of the figure. Although set E

Table 1
Energy E and symmetry k of low-lying excitations for a Mn_{12}-acetate exchange model with different parameter sets. Exchange constants are given in Kelvin [K]. The GS has spin $S = 10$ in all five cases. No energetic correction is applied for uniaxial anisotropy of the cluster.

	(A) [6]		(B)		(C)		(D) [9]		(E) [10]	
	$J_1 = 67.2$, $J_2 = 61.8$, $J_3 = 7.8$, $J_4 = 5.6$		$J_1 = 64.5$, $J_2 = 60.3$, $J_3 = 4.2$, $J_4 = 6.3$		$J_1 = 64$, $J_2 = 65$, $J_3 = 11$, $J_4 = 4$		$J_1 = 119$, $J_2 = 118$, $J_3 = -8$, $J_4 = 23$		$J_1 = 115$, $J_2 = 84$, $J_3 = -4$, $J_4 = 17$	
	E [K]	k	E [K]	k	E [K]	k	E [K]	k	E [K]	k
$S = 8$	56.52	π	58.07	π	57.13	π	68.12	π	78.39	π
	59.49	π	61.08	π	60.18	π	69.81	0	82.26	0
	61.07	0	61.78	0	62.37	0	73.55	π	83.49	π
$S = 9$	28.48	$\pm\pi/2$	29.15	$\pm\pi/2$	28.92	$\pm\pi/2$	33.99	$\pm\pi/2$	39.13	$\pm\pi/2$
	44.47	π	40.71	π	48.22	π	35.76	π	45.43	π
	91.46	0	81.82	0	102.96	0	65.11	0	77.12	0
	119.67	$\pm\pi/2$	113.42	$\pm\pi/2$	132.51	$\pm\pi/2$	174.55	$\pm\pi/2$	124.63	$\pm\pi/2$
	159.61	π	154.43	π	175.62	π	267.13	π	179.93	π
	304.45	0	297.02	0	308.05	π	501.03	0	436.52	0
$S = 10$	293.74	$\pm\pi/2$	285.63	$\pm\pi/2$	295.02	$\pm\pi/2$	507.87	π	435.95	π
	297.30	π	289.27	π	297.79	π	509.01	$\pm\pi/2$	436.83	$\pm\pi/2$
$S = 11$	285.58	0	274.17	0	287.41	0	510.38	0	429.66	0
	303.23	$\pm\pi/2$	313.84	$\pm\pi/2$	290.80	$\pm\pi/2$	696.91	$\pm\pi/2$	537.96	$\pm\pi/2$
$g_{\rm eff}$	1.935		1.935		1.92		2.12		2.1	

[10] yields qualitative agreement with the lowest $S = 9$ excitations, it is not only inconsistent with χ, but also fails to explain the magnetic excitations observed by INS around 30 meV [6].

Parameter sets A, B and C all provide qualitative agreement with the five $S = 9$ excitations, and the lowest $S = 11$ excitation, observed by INS. Set A yields the best quantitative agreement [6], while B and C yield an estimate of the error bars: although the individual J_i values differ by no more than 3.2 K, the low-lying $S = 9$ levels may shift by as much as 16 K (1.4 meV) from set A to set C. This demonstrates the high sensitivity of the excitation spectrum to small changes in the exchange constants.

Transitions from the $S = 10$ GS to states with $S \leq 8$ are not observable by INS due to selection rules. However, our results predict further low-lying excitations with $S < 9$. In particular, the $S = 8$ excitations in Table 1 may be interpreted as scattering states of a pair of the lowest $S = 9$ states ($k = \pm\pi/2$).

In summary, we have determined the microscopic exchange parameters of Mn_{12}-acetate as $J_1 \approx J_2 \approx 65$ K, and J_3, $J_4 \approx 5$–10 K. Earlier proposals [5,9,10] are inconsistent with the magnetic susceptibility, and do not match our new INS results. Further improvements to the optimal parameter set would require a treatment of the uniaxial anisotropies at the single-ion level, which would be expected to reduce the spread of the $S = 9$ levels, thereby improving agreement with the INS data.

Acknowledgments: This work was supported by the Swiss National Science Foundation, the TMR programme Molnanomag of the European Union (No: HPRN-CT-1999-00012), and by the Deutsche Forschungsgemeinschaft through grant SU 229/6-1.

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